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Description

This invention relates to the use of esterified epoxide-extended polyols (EEEPs) as non-digestible, non-caloric fat substitutes (fat mimetics) for cooking and in food compositions. The EEEPs have good organoleptic characteristics and acceptable levels of resistance to overall digestibility as measured by rat feeding studies. The EEEPs to which the invention relates may be said to have the formula $[P(OH)_{a+c}\text{-}(EPO)_n(FE)_b]$, where P is a polyol having a = 1 - 8 primary hydroxyls, and C = 0 - 7 secondary plus tertiary hydroxyls, with a + c being in the range of 3 - 8, EPO is a C_3 - C_6 epoxide, FE is a fatty acid acyl moiety having the formula RCOOH where R has 7 to 23 carbon atoms, n is equal to or greater than a, and where greater than 95% of the primary hydroxyls of the polyol have been converted to secondary or tertiary hydroxyls, and $2 < b \leq a + c$, and are resistant to hydrolysis by pancreatic lipase. The resultant EEEPs may have physical properties ranging from a liquid oil, through fats and greases. They are useful in food formulations and cooking as they have good mouth feel and characteristics similar to vegetable oils and fats. Being relatively non-absorbable, non-digestible, and non-toxic they may be substituted for natural or processed oils and fats, but have low caloric value.

Background:

The accumulation of medical evidence in recent years regarding the adverse health implications of high fat diets, principally heart attacks, atheriosclerosis and overweight, has caused consumers to become extremely concerned about their diets. It is estimated that between 70 - 80% of U.S. adult females follow a weight reducing diet at least once a year. Men are also concerned about their weight and cholesterol levels. The concerns of both men and women have given rise to diet fads, diet drinks especially in the soft drink, wine and beer industry, and exercise programs and health clubs.

Common obesity is one of the most prevelant metabolic problems among people today. Fats and oils are necessary for balanced nutrition. However, the average consumer simply consumes more than is needed for proper nutrition. Fat, at 9 calories per gram, as compared to 4 calories per gram for carbohydrates or proteins, is the most concentrated dietary energy form. It is estimated that fat constitutes about 40% of the total calories in the typical western diet. Fats are consumed directly in meats, spreads, salad oils, and in natural produce such as nuts and avocados. Fats and oils are consumed as a result of absorption or incorporation in the foods during baking and frying. The vast increase in consumption of fast foods is a major contributor to the increase in the amount of dietary fat since fast foods rely extensively on frying processes employing fats and oils. In addition, the snack food industry uses large amounts of fats and oils in the production of potato chips, corn chips and other snack items. For example, in 1981 the USDA estimated approximately 12 billion pounds of fat and oil were used in edible products, predominately baking, frying fats, margarine, salad oil and/or cooking oil.

There is thus a clear indication that there is an enormous potential health food market for a fat substitute or fat mimetic that is either entirely non-digestible, or has reduced caloric value. Many nutritionists believe that Americans typically rely on fats for too large a proportion of calories in their diet. The National Research Council, for example, has recommended that Americans reduce the proportion of their dietary calories coming from fats from 40% to at least 30%. Replacement of fats in the diet with non-caloric substitutes is a more efficient way of reducing caloric intake than replacing sugar or carbohydrates because gram for gram, the substitution of non-caloric fat substitutes is more than twice as effective as reducing carbohydrate content with such things as saccharine or Nutra-sweet.

One of the difficulties in eliminating fat from the diet is the fact that fats and oils are all-pervasive in food products. In part, this is because they play an important role in the organoleptic acceptability of food products. For a fat substitute to be acceptable, it must be non-digestible, that is, not hydrolyzed in the digestive tract. In addition, it should not be directly absorbed through the intestinal wall. While some types of fat substitutes may be non-digestible, they are not of sufficiently high molecular weight to prevent them from being absorbed through the intestinal wall. The threshold molecular weight of non-absorbability for lipophilic molecules appears to be about 600.

In addition, the fat substitute must itself be non-toxic at high levels of ingestion. It must contain no toxic residues or impurities. To the extent that a fat substitute may be partially hydrolyzed in the digestive tract, any hydrolysis products must be non-toxic and/or metabolizable. If metabolizable, they should have very low caloric value. In general, fat substitutes must be without any serious medical side affects.

The fat substitutes must also have good organoleptic qualities of mouth feel and have no taste. In addition, fat substitutes must have appropriate physical properties for use in food compositions. That is, they should be liquids or solids depending on whether they are used as oil or shortening substitutes, and

where used for cooking, must be thermally stable. While certain polysaccharide gums have been used as thickening agents, bulking agents or fillers in low-calorie foods, they can give a product a "slimy" mouth feel and are unsuitable for cooking as they have no thermal stability.

Acceptable synthetic fats would be added in large quantities (30-60%) to salad oils, cooking oils, margarines, butter blends, mayonnaise, shortenings and the like to create a new class of low-calorie products. While "low calorie" mayonnaise and salad dressings are presently available, the reduction in calories is achieved by increasing the water content with a corresponding loss in the organoleptically "rich" taste of such products.

A current review of the field is found in a feature article entitled "Getting The Fat Out - Researchers Seek Substitutes For Full-Fat Fat" JAOCS, Vol. 63, No. 3, (March 1986) pp. 278-286, 288.

One prior art proposed fat substitute is sucrose polyester (SPE), shown in U.S. patents 3,600,186 (Matson, et al. 1971), 3,521,827 and 3,963,699 (Rizzi, et al., 1976) of Proctor & Gamble. The SPEs are produced by the reaction of a monosaccharide, disaccharide or sugar alcohol having a minimum of four hydroxyl groups with fatty acids having from 8-22 carbon atoms. It was reported in "Chemical and Engineering News" (July 26, 1982, page 32) that incorporating SPE as a partial replacement of the fats in the diets of ten obese patients dropped their caloric intake while satisfying their perceived need for fats. An additional benefit was the lowering of serum cholesterol, low density lipo-protein and triglycerides, all of which have been implicated in artery hardening diseases. However, SPE has the serious disadvantage of causing diarrhoea, and plasma vitamin A and vitamin E levels are decreased.

The process for production of SPE is basically a methanolysis followed by esterification and extraction. The SPE process requires long reaction time with alternating additions of fresh transesterification catalyst and excess methyl soybean fatty acid ester (RCO_2Me). Temperature control is critical because sucrose will char at its melting point of 185C. Further, in order to solubilize sucrose in the esterification solution, it must be added slowly as a micron-sized powder (produced by reduction of sucrose crystals in a hammermill) to a solution of RCO_2Me containing half as much alkali metal soap as sucrose. After the sucrose is partially esterified, excess RCO_2Me is added and the mixture heated at 145C for 8-12 hours. The fatty ester starting material, RCO_2Me, is not made in a continous process. Rather, it is made in a batch process and must be washed with water to recover all the glycerol. Commercial cane sugar must be reduced to a consistency of fine talcum powder, on the order of 50 microns or below in order to promote its disolution in the reaction solution. Two stage addition of RCO_2Me is necessary to prevent disproportionation to sucrose, which will char, and sucrose higher esters. For each pound of SPE made, one pound of RCO_2Me must be cleaned up and recycled. Because a large excess of RCO_2Me is used, the isolation of SPE is a complex process necessitating liquid-liquid extractions at OC with methanol or ethanol to remove unreacted RCO_2Me. A final extraction with hexane and clay bleaching is necessary to produce a light-colored product. The major yield loss occurs during the purification process.

Patent 3,521,827 discloses a preparation of SPE by means of a solvent-free interesterification using phenyl esters. However, phenol is liberated during the reaction. Since phenol is extremely toxic and caustic, it contaminates the product and is very difficult to separate. Accordingly, this process did not prove satisfactory for synthesis of SPEs for the food industry. Patent 3,963,699 calls for solvent-free transesterification involving heating a mixture of the polyol containing four hydroxyls, fatty acid lower alkyl ester, and alkali metal fatty acid soap in presence of a basic catalyst to form a homogenous melt, and subsequently adding to the reaction product of that heated mixture excess fatty acid lower alkyl esters to obtain the SPE.

U.S. patent 4,034,083 also to Proctor and Gamble discloses fortification of the SPEs with fat-soluble vitamins to form pharmaceutical compositions for treating or preventing hypercolesterolemia in animals, and for use in low calorie foods. This mixture is required because eating SPE causes vitamin depletion as noted above.

U.S. patent 3,818,089 indicates that the C_{12}-C_{18} ether analogs of glycerides, glycerine alkyl ethers are not digestible.

As shown in C. U. Werl et al, Food Cosmet. Toxicol., 9 (1971) p. 479, monopropylene glycol (MPG) can be ingested with no harmful effects. It is metabolized by the same metabolic pathways used by carbohydrates. MPG is currently used as a humectant in shredded coconut and in moist cake mixes. Ethylene oxide and propylene oxide-based food additives, such as propylene glycol mono-stearate, are recognized food additives, with allowable limits being prescribed by code.

Booth, A., and Gros, A., in a paper entitled Caloric Availability and Digestibility of New-Type Fats, Journal of the American Oil Chemists Society, Vol. 40, October 1963, pp. 551-553, disclose that in rat feeding studies amylose palmitate, amylose stearate and amylose oleate are only 17-29% digested. A related prior paper of Gros, A., and Feuge, R., entitled Properties of the Fatty Acid Esters of Amylose,

Journal of the American Oil Chemists Society, Vol. 39, January 1962, pp. 19-24 discloses that these esters do not have sharp melting points and are extremely viscous when melted. The densities were somewhat greater than those of corresponding free fatty acids and glycerides. While the interest was for use as dip-type coatings in both foods and non-foods, no information appears to be available concerning the ability of these compounds to mimic sensory and functional properties of triglyceride fats in foods.

Mangold and Paltauf extensively reviewed ether lipids in their book Ether Lipids, Academic Press 1983. They report that trialkyl glycols having long alkyl chains are not hydrolyzed or absorbed when fed to rats. These long chain trialkylated glycols are reportedly non-toxic and do not interfere with absorption of fats and fat soluble vitamins. However, they are oxidized much more easily than normal fats having comparable acyl chains, so stability appears to be a problem. Further, these compounds are difficult and expensive to prepare.

Canadian patent 1,106,681 issued to Swift and Company in 1981 relates to dialkyl glycerol ethers which are absorbed only in small amounts when fed to rats. Blends are said to exhibit the physical and organoleptic properties of conventional fats.

U.S. Patent 2,962,419 discloses esters of neopentyl type alcohols such as pentaerythritoltetracaprylate. The alcohols contain from 1-8 hydroxyl radicals and include at least one neopentyl nucleus while the fatty acids contain at least four carbon atoms. They were shown to be non-hydrolyzable by pancreatic lipase. Rats fed with these esters had lower levels of lipids in their serum. However, in demand feeding studies, rats which received these neopentyl alcohol esters ate more food than the control rats and thus there was no difference in weight gain among the two groups. Accordingly, it is possible that fat craving is stimulated by these compounds rather than satisfied.

Retrofats are esters of fatty alcohols with tricarboxylic acids. It is reported that they are not hydrolyzed by pancreatic lipase and thus may have potential as non-absorbable fat substitutes. However, increased stool bulk resulting from ingestion of the non-absorbable retrofats is reported to be a potential drawback.

Alkyl esters, such as dodecyl ester of 2,3-ditetradecyloxypropionic acid have been suggested as a fat substitute but were found to be metabolized and absorbed in in vivo rat study experiments. The alkyl ester group was split off first, followed by the alkyl ether groups.

As reported in JACS, Vol. 8 (1958) pp. 6338 ff and JAOCS, Vol. 36 (1959) pp. 667 ff, the USDA has synthesized a number of diglyceride esters of short chain dibasic acids for potential application in foods. Distearin glyceride esters of dicarboxcylic acids were found to be poorly digested and utilized by rats. Distearin adipate was almost completely non-digested while adipostearin was only 58% digested in rat feeding trials. In contrast, the oleostearin and dolein esters of dicarboxylic acids were more digestible and utilized. The symmetrical diglyceride esters of fumaric, succinic and adipic acids are more viscous than cottonseed oil and coconut oil. These may have use as pan greases, slab dressings or surface coatings for foods.

U.S. Patent 3,579,548 to Procter and Gamble in 1971 discloses uses of triglyceride esters of alpha-branched carboxylic acids as low calorie fats. These esters exhibited a coefficient of absorbability ranging from about 0-50 as compared to 90-100 for ordinary triglycerides. It is postulated that the alpha-branched carboxylate structure prevents the compounds from being hydrolyzed by pancreatic enzymes. Proposed uses are as fat replacements in salad oil, mayonnaise, margarine and dairy products.

Polyoxyethylene stearate is an emulsifying agent with fat like properties that yields only 4.2 kcal/gram when ingested. The molecule is hydrolyzed to stearic acid which is metabolizable, and to polyoxyethylenediol which is excreted unchanged. The use of fat-like emulsifying agents as low calorie fat substitutes has been suggested in the literature.

U.S. Patent 3,337,595, issued to Nalco Chemical in 1967, discloses a method of producing fatty acid esters of polyoxypropylated glycerol of the formula glycerol (propylene oxide)$_n$(fatty acids)$_m$, which from the molecular weight values in the patent result in n = 9 - 16 and m = 1 or 2. These esters are disclosed to be useful for controlling, suppressing and/or preventing foaming of aqueous systems having foaming tendencies in industrial processes. Illustrative types of aqueous systems are cellulosic suspensions involved in the manufacture of paper, sewage disposal systems, detergent containing systems, saponin-containing systems, protein containing systems and the like. 1,2-propylene oxide is adducted on glycerol to produce a polyoxypropylated glycerol (POG) with a molecular weight in the range of 600-1,000. Fatty acid esters are prepared by stoichiometric esterification of the POG with saturated or unsaturated aliphatic monocarboxylic acids having chain lengths of 12-22 carbons. The esterification process occurs in the range of 200-240C under a vacuum on the order of 30-50 mm mercury. Specific examples are directed to stearic acid diesters of polyoxypropylated glycerol having a molecular weight of 700. An emulsifier is required in the anti-foaming formulations, the specific examples being directed to polyoxyethylene glycol 400 di-oleate. The monocarboxylic acids used to form the diesters are those having C_{12-22} carbons. There is no specific

disclosure of a triester or of complete etherification with propylene oxide. There is also no disclosure of the use of the diester compounds as fat substitutes in food products.

Gibson, U. H., and Quick, Q., in a paper entitled The Average Molecular Structure of Base-Catalyzed Low-Mole Adducts of Propylene Oxide to Glycerin, J. Applied Polymer Sci., Vol. 14 (1970) pp. 1059-1067 indicate that with a molar ratio of glycerin (G) to propylene oxide (PO) of 1:3, 63% of the adduct product will have all three hydroxyls propoxylated, with 1:4, 92% are propoxylated, and with a ratio of 1:5 all the original hydroxyls will be propoxylated.

It is clear that there is a great need in the art for improved fat substitutes that are easy to synthesize and do not have the disadvantages of the prior art proposed compounds.

Japanese patent publication 55-79313 describes skin or hair cosmetics containing an esterification product of a polyether polyol having the general formula

$$\begin{array}{l} CH_2O(CH_2\overset{\overset{CH_3}{|}}{C}HO)_{n1}(CH_2CH_2O)_{m1}H \\ | \\ CHO\ (CH_2\overset{\overset{CH_3}{|}}{C}HO)_{n2}(CH_2CH_2O)_{m2}H \\ | \\ CH_2O(CH_2\overset{\overset{CH_3}{|}}{C}HO)_{n3}(CH_2CH_2O)_{m3}H \end{array}$$

where n1, n2 and n3 = 0 20; m1, m2 and m3 = 0 20 and n1+n2+n3+m1+m2+m3 = 3 70, and a higher linear saturated fatty acid and/or a higher branched chain fatty acid and/or a higher hydroxy saturated acid.

Japanese patent publication 55-160710 describes cosmetics for use with skin or hair derived by blending one, two or more kinds of polyvalent esterification product(s) obtained by bringing about an esterification reaction between (1) a polyether polyol obtained by modifying a tetrahydric or greater alcohol by the addition to said alcohol of ethylene oxide or (and) propylene oxide (number of mols added into each molecule of the polyhydric alcohol: ethylene oxide, 0 to 20 mols, propylene oxide, 0 to 20 mols; the sum of the number of mols of ethylene oxide and propylene oxide added is not below the number of OH groups on the polyhydric alcohol) and (2) one or two or more fatty acid(s) selected from the group consisting of higher straight chain saturated fatty acids, higher side chain saturated fatty acids, higher hydroxy saturated fatty acids, and higher unsaturated fatty acids.

This invention provides the use, as a reduced calorific substitute for an edible oil or fat, of esterified epoxide-extended polyols (EEEPs) which may be used alone as cooking oils, fats or waxes, or as part of food compositions, as a partial or total substitute for fats or oils.

The invention also provides improved food compositions and products employing the fat substitutes of this invention.

The esterified epoxide-extended polyols (EEEPs), employed in this invention have good organoleptic characteristics, are substantially resistant to intestinal absorption, and do not appreciably hydrolyze in the digestive tract. Both they and their hydrolysis products are non-toxic.

The structure of the non-digestible fat substitutes of this invention may be generally characterized as $P(OH)_{a+c}(EPO)_n(RCOOH)_b$, where: P(OH) is a polyol having a = 1 - 8 primary hydroxyls and c = 0 - 7 secondary plus tertiary hydroxyls, with a + c being in the range of 3 - 8, EPO is a C_3-C_6 epoxide; n is the minimum epoxylation index average number having a value generally equal to or greater than a and is a number sufficient that greater than 95% of the primary hydroxyls of the polyol are converted to secondary or tertiary hydroxyls; RCOOH is a fatty acid acyl moiety of 8 to 24 carbon atoms; and b is an average number in the range of $2 < b \leq (a + c)$.

According to the present invention there is provided the use, as a reduced calorific substitute for an edible oil or fat, of a mixture of epoxide-extended polyol esters obtainable by the reaction of (A) the product of reacting n moles of a C_{3-6} epoxide per mole of a polyol having the formula $P(OH)_{a+c}$ where a is the number of primary hydroxyl groups in the polyol and is in the range 1 to 8, c is the total number of secondary and tertiary hydroxyl groups in the polyol and is in the range 0 to 7, the total of a+c being in the range 3 to 8; n is equal to or greater than a, and greater than 95% of the primary hydroxyl groups in the polyol are replaced in said product by secondary or tertiary hydroxyl groups, with (B) b moles, per mole of said product, of a fatty acid having the formula RCOOH where R has 7 to 23 carbon atoms and b is greater

than 2 but not greater than a + c.

The invention further provides an edible composition e.g. a salad dressing, margarine, butter blend, mayonnaise or shortening, containing fat-type and non fat-type ingredients, wherein at least a part, e.g. from about 10 to 100% of the fat-type material of the composition, comprises a mixture of epoxide extended polyol esters as defined above.

The invention also provides a composition comprising a mixture of fat-type ingredients suitable for use as a cooking oil or fat or in the preparation of low caloric food compositions, said mixture comprising an edible oil or fat and at least 10% by weight, based on the total weight of the mixture, of a mixture of epoxide-extended polyol esters as defined above.

In a preferred embodiment, the mixture of epoxide-extended polyol esters is obtained by a method comprising the steps of:-

(a) reacting said polyol of the formula $P(OH)_{a+c}$ in the presence of a base catalyst with said C_3-C_6 epoxide, for a period of time sufficient to provide a polyepoxide-extended polyol having a minimum epoxylation index average number n which is not less than a and wherein greater than 95% of the primary hydroxyls of said polyol are converted to secondary or tertiary hydroxyls; and

(b) reacting said epoxide-extended polyol with at least one said fatty acid, RCOOH, to product said epoxide-extended polyol esters.

In one prefered aspect of this embodiment of the invention, the method of forming the mixture includes the steps of:-

(a) splitting a natural fat or oil selected from soybean oil, rapeseed oil, tallow, cottonseed oil, coconut oil, palm oil, babassu oil, corn oil, lard, fish oil, olive oil, peanut oil, safflower seed oil, sesame seed oil, jojoba oil and sunflower seed oil and mixtures thereof to form glycerol and one or more fatty acids RCOOH where R is a C_7-C_{23} group;

(b) separating the glycerol from said fatty acid; and

(c) employing said glycerol in the base catalysed addition reaction referred to above.

It is preferred that the acyl groups of the EEEPs are of sufficient size to prevent absorption through the walls of the digestive system, and that the epoxylation index is sufficiently high to prevent a substantial degree of hydrolysis.

In one aspect of the invention, n is above about 2 and preferably in the range of 2 - 8.

Preferably the polyol has 3 - 8 hydroxyl groups. More preferably it is glycerol. Particularly preferred are acylated, propylene oxide-extended glycerols wherein n is above about 2, and preferably in the range of 2 - 8, especially those wherein the acyl groups have 8 to 24 carbon atoms and which have an in vitro pancreatic lipase hydrolysis index relative to olive oil below about 10.

In one preferred embodiment the EEEPs comprise triacylated propoxylated glycerols having a propoxylation index above about 2 and preferably about 5 or above, and wherein the acyl groups have 8 to 24 preferably 14 to 18, carbon atoms, said EEEPs having a lipase hydrolysis index (relative to olive oil) below about 10.

Suitable polyols include sugars, glycerides or saccharides which are reacted (etherified) with C_3-C_6 epoxides such as propylene oxide, butylene oxide, isobutylene oxide, pentene oxide, and the like to produce epoxide-extended polyols (EEPs) having an epoxylation index which is preferably above about 2, more preferably in the range of 2 - 8. Sugars may be selected from glucose, mannose, galactose, arabinose, xylose, sorbitose, amylose, and the like.

We prefer the polyol is glycerol, with the resultant formula being:

$$\begin{array}{l} CH_2-O-(CR_1R_2-CR_3R_4-O)_d-(COR_5)_x \\ | \\ CH-O-(CR_1R_2-CR_3R_4-O)_e-(COR_5)_y \\ | \\ CH_2-O-(CR_1R_2-CR_3R_4-O)_f-(COR_5)_z \end{array}$$

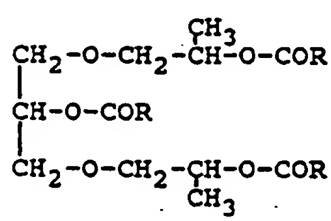
where d + e + f = n as defined above, x + y + z = b as defined above, R_1 = R_2 = H, R_3 = H or alkyl, R_4 = alkyl, and R_5 = C_{7-23}, preferably C_{13-17}. Where propylene oxide is employed as the epoxide R_1, R_2 and R_3 are H, R_4 is Me, and d + e + f, the epoxylation (propoxylation) index, is 2 - 8, preferably about 3 - 5, based on in vitro pancreatic lipase activity relative to olive oil.

The epoxylation index and acyl chain length must be such that the resultant EEEPs are resistant to digestive tract absorption and in vivo digestion by non-specific digestive or lingual lipases. There are two factors to be considered. The first is the epoxylation index for non-digestability, the second is acyl chain length for non-absorption. Where n = 4 is found to be the suitable in vivo threshold for non-digestability, then the cutoff of the R_5 acyl chain length for direct absorption could be as low as C_7 (the octanoate ester). This species (using glycerol and propylene oxide) would have an average MW of 702, but since there is a MW distribution in the mixture, species of MW of 586 and 644 would be present.

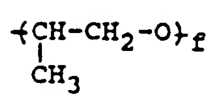
The esters of tertiary alcohols (R_3 = R_4 alkyl) or secondary alcohols with bulky substituents can provide good protection from lipase hydrolysis. For example: 1,2-epoxybutane (R_4 = Et), 2,3-epoxybutane (R_2 = R_4 = Me), both butylene oxide; 1,2-epoxy-3-methylpropane (R_3 = R_4 = Me), isobutylene oxide; 1,2-epoxycyclohexane; and the like, may be used.

It should be understood that the epoxylation index encompasses the mixtures produced by the base catalyzed reaction of the polyol with the epoxide. Thus, where glycerol and propylene oxide are used with C_{16}-C_{18} fatty acids, we have found that as compared to olive oil as a representative substrate having a rate of in vitro lipase reactivity of 100, the propoxylation index of 2 or greater has a hydrolysis rate value on the order of 20-30% of the olive oil. By non-digestability we mean a rate below about 20%, preferably 10%. Thus, food products could be made or cooked in a mixture of natural fats and the synthetic fat mimetics of this invention blended in proportion to provide any predetermined amount of fat caloric value. Where n is 4-5, the relative lipase rate is zero. Depending on the organoleptic qualities desired, the amount of substitution would range from a few percent, to give fractional reduction in caloric value, to entire substitituion for a non-caloric product. Conversely, where the EEEP product has a relative lipase rate close to 20, different amounts of the EEEP fat substitute of this invention could be used in the blend to achieve a desired organoleptic quality or provide a particular cooking use, (e.g., oil vs. fat).

For example, in the case of glycerol and propylene oxide where a = 2, c = 1, n = 2 and b = 3, the resulting principal compound is triacyl-1,3-di-(2-hydroxypropyl) glycerol:



Conversely, where n is greater than a, e.g., n = 3 or more for glycerol, the EEEP compounds of this invention will include polyepoxides in the expoxide-extended interlink between the polyol and the acyl ester moieties. Thus, for propylene oxide, there will be present



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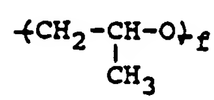

links, where f is 2 or more. The latter linkages predominate. While we do not wish to be bound by theory, we believe that the non-digestibility of the EEEPs of this invention is due to the alcohol ester linkage being secondary rather than primary.

Acylation with one or more C_{8-24} fatty acids produces an end product ester with physical properties ranging from a liquid oil, through fats and greases, and ultimately to waxes. The resultant EEEPs are useful in food formulations and for cooking as they have good mouth feel and characteristics similar to vegetable

oils and fats. Being relatively non-absorbable, non-digestible, and non-toxic they may be substituted for natural or processed oils and fats, but have no caloric value.

Examples of such fatty acids are caprylic, capric, lauric, myristic, myristoleic, stearic, palmitic, palmitoleic, ricinoleic, linoleic, linolenic, eleaostearic, arachidic, behenic, erucic, oleic, and/or heptadecanoic acid. The fatty acids can be derived from suitable naturally occurring or synthetic fatty acids and can be saturated or unsaturated, including positional and geometric isomers, depending on the desired physical properties, e.g., liquid or solid, of the fat compound.

Fatty acids per se or naturally occurring fats and oils can serve as the source for the fatty acid component. For example, rapeseed oil provides a good source for C_{22} fatty acid. C_{16-18} fatty acids can be provided by tallow, soybean oil, or cottonseed oil. Shorter chain fatty acids can be provided by coconut, palm kernel oil, or babassu oils. Corn oil, fish oil, lard, olive oil, palm oil, peanut oil, safflower seed oil, sesame seed oil, jojoba oil and sunflower seed oil, are examples of other natural oils which can serve as the source of the fatty acid component. Among the fatty acids, those that are preferred have from about 14 to about 18 carbon atoms, and are most preferably selected from the group consisting of myristic, palmitic, stearic, oleic, and linoleic. The preferred sources for the fatty acid components are natural fats and oils which have a high content of these fatty acids, e.g., soybean oil, olive oil, cottonseed oil, corn oil, tallow and lard.

Best mode examples of the invention include acylated propoxylated glycerol compound mixtures (APGs) of the formula $[G(PO)_n(FE)_b]$, where G is glycerol (i.e. a = 2 and c = 1 in the $P(OH)_{a+c}$ formula above), PO is Propylene Oxide, FE is a fatty acid ester moiety, the average propoxylation number n is in the range of 2 - 5, and b is an average number between above 2 and 3. Suitable fatty acids include mixtures of palmitic acid or heptadecanoic acid with oleic acid. These APGs are resistant to hydrolysis by porcine pancreatic lipase, the dominant enzyme in fat digestion, in vitro.

Even where the fatty acid moieties are hydrolyzed off the EEEPs and APGs of this invention, no outward sign of toxicity of the resulting EEP was observed in our study. Indeed, even propylene glycol which would be released on cleavage of the EEP ether linkage is given GRAS (Generally Recognized as Safe) status by the FDA. Propylene glycol and its derivatives are used at low levels in the food industry, e.g. as solvents for flavors and pharmaceuticals, and in baked goods, salad dressings and sauces.

The EEEP mixtures employed in the present invention may be prepared by a process which involves a base (preferably alkali metal) catalyzed reaction of the polyol with the epoxide. As noted in the Gibson and Quick paper, supra, the base catalysis opens the oxirane ring of the propylene oxide in the addition reaction to provide a predominance of secondary hydroxyl groups, on the order of 98% secondary to 2% primary. We prefer, in the case of glycerol, to start with a fat such as soybean oil, split it to form glycerol and RCO_2H, and separate the glycerol from the fatty acid. This provides the glycerol for the base catalyzed propoxylation addition reaction. The resultant $G(PO)_n$, preferably n = 2 - 5, may then be reacted rapidly at high temperature, between about 100 to 200 °C, in the presence of paratoluene sulphonic acid (PTSA) with a stoichiometric amount of the soybean oil fatty acid to produce the resultant APGs mixture product. The APGs product can be refined and bleached in a conventional manner, e.g. with alkali and clay, to provide a clean product of low color and low acid value.

Detailed Description of the Best Mode

The following detailed description is by way of example, not by way of limitation, of the principles of the invention to illustrate the best mode of carrying out the invention.

In this example, the epoxide (EPO) is represented by propylene oxide (PO), the polyol $P(OH)_{a+c}$ by glycerol (G), and the esterified fatty acid acyl moiety (FE) by a mixture of either palmitic or heptadecanoic acids with oleic acid, to produce a food oil/fat substitute/mimetic of the formula $[G(PO)_n(FE)_b]$, where n = 2 - 5 and b = 3. With the addition of 5 PO units, all the original polyol (in this example a triol) hydroxyls will have been etherified (in this example propoxylated).

EXAMPLE 1

I. Propoxylated Glycerol Synthesis

A. Catalyst Preparation

A catalyst solution for the propoxylation reaction is prepared to provide .25 wt % K^+ in 6000 gms final propoxylated product. To prepare the catalyst, 27.59 grams powdered potassium hydroxide and 300 grams

glycerol, G, are charged to a 1000 cc rotary evaporation flask and heated under nitrogen at 75-80C with stirring for about one hour. The catalyst goes into solution leaving a cloudy product which is stripped on a rotary evaporator at 60-70C/5mm Hg for one hour to remove water. The theoretical water loss is 12.98 grams. The catalyst solution (314.62 gms) is added to a dry, nitrogen flushed 2-gallon stainless steel stirred reactor.

B. Propoxylation Reaction; 1:3 G:PO

To prepare propoxylated glycerol with three oxypropylene units the initial glycerol charge is 2073.32 gms (i.e., 1773.32 gms charged as free glycerol, and 300 gms added with the catalyst charge). The remaining 1773.32 gms glycerol (MW = 92.1 gm/mole) was added to the reactor under a continuous purge with dry nitrogen. The reactor was heated to 70-75C and nitrogen pressure was adjusted to 20 psig. An initial charge of 500 grams propylene oxide, PO, (MW = 58.08 gm/mole) was added to the reactor, and the reaction exotherm was allowed to carry the temperature up to 90C. After the reaction was initiated, the temperature was adjusted to 90-95C and the remaining dry propylene oxide was added on a pressure demand basis over an 18 hour period. A pressure demand control valve system was used to control the addition rate. A reference pressure was set at 60 psig. If the reactor pressure dropped below this pressure the control valve opened and more propylene oxide was charged to the reactor. When the pressure increased to greater than 60 psig, the valve closed. The propylene oxide was contained in a yoke that was suspended on a weight load cell, thereby permitting the charging of the correct amount of propylene oxide. To prepare propoxylated glycerol with three oxypropylene units the total propylene oxide charge is 3926.68 grams. Since the yoke had a 552 kPa gauge (80 psig) nitrogen pressure head, the overall reactor pressure increased to 552 kPa gauge 80 psig when all the propylene oxide was pushed out of the load cell yoke into the reactor. After all the propylene oxide had been added, the reaction mixture was allowed to cook out for an additional 4-6 hours to insure complete reaction.

When the reaction was complete, the product was removed hot from the reactor and was treated with Magnesol[R] (4 grams per 250 grams product) for two hours at 100-110C in order to remove the K^+ catalyst. The resulting product was vacuum filtered through a Cellite[R] (purified diatomaceous silica) bed at 60-80C to provide the pure oligomeric polyol. Hydroxyl Number, VPO molecular weight, Gel Permeation Chromatography (GPC) analysis, and ^{13}CNMR were used to characterize the hydroxy propoxylated glycerols mixture, HPGs. For the HPGs with three oxypropylene units, polydispersity by GPC analysis is 1.19 and the molecular weight calculated from the Hydroxyl Number is 266 gms/mole.

II. Synthesis of APGs (Tri-acylated HPGs).

In a typical synthesis, a solution of 0.035 moles of redistilled acyl chlorides (a mixture of a 1:5 molar ratio of either palmitoyl or heptadecanoyl chloride to oleoyl chloride) in dry chloroform (20 ml) is added dropwise to a stirred solution of 0.01 mole of the HPGs in dry chloroform (20 ml) and dry pyridine (6 ml). The addition is made at room temperture, under an atmosphere of dry nitrogen, and stirring is continued for a further 24 hours. A phase separation occurs in the reaction vessel. At the end of the reaction, the mixture is added to water (500 ml) and extracted several times with petroleum ether (3 X 500 ml). The combined organic phase is then washed with water (2 X 500 ml), dilute aqueous HCl (2 X 500 ml), water (2 X 500 ml), aqueous potassium bicarbonate (2 X 500 ml), and then water (2 X 500 ml), and dried over anhydrous sodium sulphate before evaporation of the solvent. Prior to column chromatography, any free fatty acids still present are methylated with ethereal diazomethane. The crude acylated propoxylated glycerol mixtures (APGs) product is purified by passage down a silicic acid column, eluting with a gradient of diethylether (0 to 100%) in petroleum ether. Overall yields for the APGs synthesis fall in the range of 59-75%. Purity and structure of the APGs product are confirmed by IR and ^{1}H NMR spectroscopy, and by Thin Layer Chromatography (TLC).

The resultant APG products are all oils at room temperature and generally a very acceptable pale yellow color, but which can be easily bleached or clarified by passing through charcoal. The APGs exhibited reverse viscosity, with the n = 1 and n = 2.2 products (see Example 2 below) being slightly more viscous than olive oil, and the n = 5 and n = 8 products slightly less viscous than olive oil. Similarly the n = 5 and n = 8 did not solidify at 5°C while the n = 1 and n = 2.2 exhibited partial crystallization at 5°C. The molecular weight ranges are determined as follows: n = 1, 884-1000; n -= 2.2, 942-1116; n = 5, 1058-1290; and n = 8, 1058-1348 assuming the trioleoyl derivatives and including 95% of the total mass of the polymeric mixtures. All exhibited organoleptically acceptable properties, having a bland oily mouth feel without being slimy.

III. In Vitro Testing of the APGs (n = 1 - 8) for Digestion by Pancreatic Lipase

EXAMPLE 2

Following the above procedure in Example 1, a number of APG products of the EEEPs of this invention were prepared in which n was varied in the range of from 1-8 by control of the amount of PO in the reaction. 100 mg of the APG fat or oil of the invention to be tested is added to 10 ml of buffer containing 1 mM, NaCl, 1 mM $CaCl_2$, 3 mM deoxycholate, 2 mM tris, and 10 g/l of gum arabic. The mixture is vigorously shaken in a capped test-tube, and the emulsion is transferred to the pH stat reaction vessel. The pH is titrated to 8.0 using a Radiometer pH stat (comprising a TTA80 titration assembly, a TTT80 titrator, and ABU80 autoburette and a pHM82 pH meter). Porcine pancreatic lipase (0.1 ml, equivalent to 1000 units of enzyme, at pH 8.0) is added, the pH rapidly re-equilibrated to 8.0, and then the reaction followed over a 20 minute period by autotitration with 50 mM aqueous NaOH. The initial, linear rate is reported as micro moles of NaOH per hour required to keep the pH constant by neutralising the free fatty acids released by the action of pancreatic lipase.

The results are given below in Table I, expressed as an average of 4 determinations, relative to olive oil as a control (100%), where the EPO is PO and the FE is as in Example I, part II.

Table I

Digestibility (Lipase Activity)	
Substrate	Relative Rate*
Control: Olive Oil	100
APGs: $G(EPO)_n(FE)_b$	
n = 0	76.2
n = 1	46.2
n = 2.2	18.9
n = 5	0
n = 8	0

* Average of four determinations.

Based on the above Table I data, at n = 3 the lipase hydrolysis rate is about 10%, and at n = 4 it is about 5%. We prefer the lipase hydrolysis rate to be below about 10%.

The corresponding acetate adducts of the tested APGs of Table I (n = 1, 2.2, 5 and 8) were assayed by Gas Liquid Chromatography (packed column) to show the distribution of polypropylene oxide units in each. The results are shown in Table II:

Table II

Distribution of Polyepoxide Units												
% Area by GLC (Packed Column)												
			G:PO									
Adduct	PG	G	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8	1:9	1:10
$G(PO)_1$	ND	31.1	46.2	19.9	2.7							
$G(PO)_{2.2}$	ND	2.1	22.7	40.5	28.0	5.9	0.7					
$G(PO)_5$	t	ND	ND	1.4	16.1	34.5	28.5	13.6	5.1	0.8		
$G(PO)_8$	t	ND	ND	ND	4.9	13.3	22.3	25.8	22.6	8.3	2.7	ND
ND = Not detectable t = trace PG = propyleneglycol G = glycol												

The above components represent 90% of the mass trace integral, except for $G(PO)_8$ where the value was 67.8% due to presence of unknown additional components, (NOT triacetin). The area % are corrected to give mass or mole % (FID response factors unknown).

Where the APGs product average molecular weight is too low, below about 600-900, it is not useful as a non-digestible fat substitute because it will be directly absorbed in the gut. We believe the non-digestibility of the APGs product of this invention is due primarily to the presence of secondary alcohol ester linkages.

IV. IN VIVO Testing.

EXAMPLE 3 FEEDING STUDIES

Sprague-Dowley weanling rats (male) were fed a laboratory chow diet containing 2.5% by weight of two different test compounds: either the n = 2.2 composition or the n = 5 composition of Example 2, each containing 18% of heptadecanoic acid as a marker, the balance of the fatty acid (acyl) moiety in the EEEP test compound being oleic acid. Total dietary lipid was kept at 10% (by weight) with 2.75% added corn oil, the laboratory chow already containing 4.5% lipid. Also, a known non-digestible marker compound, 1,2-didodecyl-3-hexadecyl glycerol, was added to the diets at 0.25% (by weight) level.

The feeding trial continued for three weeks, during which time rat body weight gain increased at a rate equal to that of control animals. No outward signs of toxicity were observed. Feces were collected and analysed for lipid content, using a GLC method based on heptadecanoic acid and 1,2-didodecyl-3-hexadecylglycerol markers. The data show the following percentage recoveries of heptadecanoic acid (HDA) in the feces:

TABLE III

Non-Digestability			
Test Compounds	%HDA as Free Fatty Acid	%HDA Still Esterified	Total Fecal HDA%
n = 2.2	12	6	18
n = 5	13	31	44

The percentages listed under %HDA as Free Fatty Acids represents the percentage of the test compound that was not absorbed, but the HDA moiety of which was hydrolyzed in the gut or in the feces by digestive enzymes or microbial action. The percentages listed under %HDA Still Esterified indicate the percentage still in original form, not hydrolyzed in gut or feces. The last column shows the total of the two preceeding columns, being the percentage not absorbed or digested.

The data show that the test compounds, particularly the n = 5 compounds (pentahydroxypropylglycerol), are suitably resistant to overall digestion, which includes hydrolysis and absorption in the upper intestine of the rat, and some hydrolysis and utilization by the microbial population of the cecum, colon, and feces.

The synthesis above involving propylene oxide can be employed for epoxylation with butylene oxide and isobutylene oxide, to produce the corresponding epoxide extended polyols which are then acylated, preferably peracylated as above-described.

It should be understood that various modifications within the scope of this invention can be made by one of ordinary skill in the art without departing from the spirit thereof. We therefore wish our invention to be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of this specification if need be.

Claims

1. The use, as a reduced calorific value substitute for an edible oil or fat, of a mixture of epoxide-extended polyol esters obtainable by the reaction of (A) the product of reacting n moles of a C_{3-6} epoxide per mole of a polyol having the formula $P(OH)_{a+c}$ where a is the number of primary hydroxyl groups in the polyol and is in the range 1 to 8, c is the total number of secondary and tertiary hydroxyl groups in the polyol and is in the range 0 to 7, the total of a+c being in the range 3 to 8; n is equal to or greater than a, and greater than 95% of the primary hydroxyl groups in the polyol are replaced in said product by

secondary or tertiary hydroxyl groups, with (B) b moles, per mole of said product, of a fatty acid having the formula RCOOH where R has 7 to 23 carbon atoms and b is greater than 2 but not greater than a+c.

2. The use as claimed in claim 1 wherein n is sufficient to impart a lipase hydrolysis rate of below about 10% compared to olive oil.

3. The use as claimed in claim 1 or claim 2 wherein n has an average value in the range 2 - 8.

4. The use as claimed in any one of claims 1 to 3 wherein R is of sufficient length that the mixture of epoxide-extended polyol esters is substantially resistant to digestive tract absorption.

5. The use as claimed in claim 4 wherein R is selected from C_{13-17} chains and mixtures thereof.

6. The use as claimed in any one of claims 1 to 5 wherein the epoxide is selected from propylene oxide, pentene oxide, 1,2-epoxybutane, 2,3-epoxybutane, 1,2-epoxy-2-methylpropane, 1,2-epoxy-cyclohexane, and mixtures thereof.

7. The use as claimed in any one of claims 1 to 6 wherein the polyol is selected from sugars, glycerol, saccharides and mixtures thereof.

8. The use as claimed in claim 7 wherein the sugar is selected from glucose, mannose, galactose, arabinose, xylose, sorbitose, amylose and mixtures thereof.

9. The use as claimed in any one of claims 1 to 8 wherein $P(OH)_{a+c}$ is glycerol, a is 2, c is 1, the epoxide is selected from propylene oxide, butylene oxide and isobutylene oxide, n has an average value of from 2 to 8, and b has an average value which is greater than 2 but not greater than 3.

10. The use as claimed in claim 9 wherein n is in the range of 2 - 5, preferably 3 - 5, and b is 3.

11. The use as claimed in any one of claims 1 to 10 wherein said mixture has been prepared by a method comprising the steps of:
a) reacting said polyol of the formula $P(OH)_{a+c}$ in the presence of a base catalyst with said C_3-C_6 epoxide, for a period of time sufficient to provide a mixture of polyepoxide-extended polyols having a minimum epoxylation index average number n which is not less than a and wherein greater than 95% of the primary hydroxyls of said polyols are converted to secondary or tertiary hydroxyls; and
b) reacting said mixture of epoxide-extended polyols with at least one said fatty acid, RCOOH, to produce said mixture of epoxide-extended polyol esters.

12. The use as claimed in claim 11 wherein said method includes the steps of:-
a) splitting a natural fat or oil selected from soybean oil, rapeseed oil, tallow, cottonseed oil, coconut oil, palm oil, babassu oil, corn oil, lard, fish oil, olive oil, peanut oil, safflower seed oil, sesame seed oil, jojoba oil and sunflower seed oil and mixtures thereof to form glycerol and one or more fatty acids RCOOH where R is a C_7-C_{23} group;
b) separating the glycerol from said fatty acid; and
c) employing said glycerol in the base catalysed addition reaction of claim 11

13. The use as claimed in claim 12 wherein $P(OH)_{a+c}$ is glycerol, a is 2, c is 1, the epoxide is propylene oxide, n has an average value above 2.2, and b has an average value above 2 but not more than 3.

14. The use as claimed in claim 12 wherein $P(OH)_{a+c}$ is glycerol, a is 2, c is 1, the epoxide is selected from butylene oxide and isobutylene oxide, n is an average value of from 2 to 8, and b has an average value which is above 2 but not more than 3.

15. An edible composition containing fat-type and non-fat ingredients, and wherein at least a part of the fat-type material of the composition comprises a mixture of epoxide-extended polyol esters obtainable by the reaction of (A) the product of reacting n moles of a C_{3-6} epoxide per mole of a polyol having the formula $P(OH)_{a+c}$ where a is the number of primary hydroxyl groups in the polyol and is in the range 1

to 8, c is the total number of secondary and tertiary hydroxyl groups in the polyol and is in the range 0 to 7, the total of a + c being in the range 3 to 8; n is equal to or greater than a, and greater than 95% of the primary hydroxyl groups in the polyol are replaced in said product by secondary or tertiary hydroxyl groups, with (B) b moles, per mole of said product, of a fatty acid having the formula RCOOH where R has 7 to 23 carbon atoms and b is greater than 2 but not greater than a + c.

16. An edible composition as claimed in claim 15 which is a salad dressing, margarine, butter blend, mayonnaise or shortening.

17. A composition comprising a mixture of fat-type ingredients suitable for use as a cooking oil or fat or in the preparation of low caloric food compositions, said mixture comprising an edible oil or fat and at least 10% by weight, based on the total weight of the mixture, of a mixture of epoxide-extended polyol esters obtainable by the reaction of (A) the product of reacting n moles of a C_{3-6} epoxide per mole of a polyol having the formula $P(OH)_{a+c}$ where a is the number of primary hydroxyl groups in the polyol and is in the range 1 to 8, c is the total number of secondary and tertiary hydroxyl groups in the polyol and is in the range 0 to 7, the total of a + c being in the range 3 to 8; n is equal to or greater than a, and greater than 95% of the primary hydroxyl groups in the polyol are replaced in said product by secondary or tertiary hydroxyl groups, with (B) b moles, per mole of said product, of a fatty acid having the formula RCOOH where R has 7 to 23 carbon atoms and b is greater than 2 but not greater than a + c.

18. A composition as claimed in any one of claims 15 to 17 wherein n is sufficient to impart a lipase hydrolysis rate of below about 10% compared to olive oil.

19. A composition as claimed in any one of claims 15 to 18 wherein n has an average value in the range 2 - 8.

20. A composition as claimed in any one of claims 15 to 19 wherein R is of sufficient length that the mixture of epoxide-extended polyol esters is substantially resistant to digestive tract absorption.

21. A composition as claimed in claim 20 wherein R is selected from C_{13-17} chains and mixtures thereof.

22. A composition as claimed in any one of claims 15 to 21 wherein the epoxide is selected from propylene oxide, pentene oxide, 1,2-epoxybutane, 2,3-epoxybutane, 1,2-epoxy-2-methylpropane, 1,2-epoxy-cyclohexane, and mixtures thereof.

23. The use as claimed in any one of claims 1 to 6 wherein the polyol is selected from sugars, glycerol, saccharides and mixtures thereof.

24. A composition as claimed in claim 23 wherein the sugar is selected from glucose, mannose, galactose, arabinose, xylose, sorbitose, amylose and mixtures thereof.

25. A composition as claimed in any one of claims 15 to 24 wherein $P(OH)_{a+c}$ is glycerol, a is 2, c is 1, the epoxide is selected from propylene oxide, butylene oxide and isobutylene oxide, n has an average value of from 2 to 8, and b has an average value which is greater than 2 but not greater than 3.

26. A composition as claimed in claim 25 wherein n is in the range of 2 - 5, preferably 3 - 5, and b is 3.

27. A composition as claimed in any one of claims 15 to 26 wherein said mixture has been prepared by a method comprising the steps of:

a) reacting said polyol of the formula $P(OH)_{a+c}$ in the presence of a base catalyst with said C_3-C_6 epoxide, for a period of time sufficient to provide a mixture of polyepoxide-extended polyols having a minimum epoxylation index average number n which is not less than a and wherein greater than 95% of the primary hydroxyls of said polyols are converted to secondary or tertiary hydroxyls; and

b) reacting said mixture of epoxide-extended polyols with at least one said fatty acid, RCOOH, to produce said mixture of epoxide-extended polyol esters.

28. A composition as claimed in claim 27 wherein said method includes the steps of:-

a) splitting a natural fat or oil selected from soybean oil, rapeseed oil, tallow, cottonseed oil, coconut oil, palm oil, babassu oil, corn oil, lard, fish oil, olive oil, peanut oil, safflower seed oil, sesame seed oil, jojoba oil and sunflower seed oil and mixtures thereof to form glycerol and one or more fatty acids RCOOH where R is a C_7-C_{23} group.
b) separating the glycerol from said fatty acid; and
c) employing said glycerol in the base catalysed addition reaction of claim 11.

29. A composition as claimed in claim 28 wherein $P(OH)_{a+c}$ is glycerol, a is 2, c is 1, the epoxide is propylene oxide, n has an average value above 2.2, and b has an average value above 2 but not more than 3.

30. A composition as claimed in claim 12 wherein $P(OH)_{a+c}$ is glycerol, a is 2, c is 1, the epoxide is selected from butylene oxide and isobutylene oxide, n is an average value of from 2 to 8, and b has an average value which is above 2 but not more than 3.

Patentansprüche

1. Verwendung einer Mischung von epoxidverlängerten Polyolester als kalorienreduziertes Surrogat für ein eßbares Öl oder Fett, erhältlich durch die Reaktion von (A) des Produktes der Reaktion von n Mol eines C_{3-6}-Epoxides pro Mol eines Polyols mit der Formel $P(OH)_{a+c}$, in der a die Zahl der primären Hydroxylgruppen im Polyol bedeutet und im Bereich von 1 bis 8 liegt, c die Gesamtzahl von sekundären und tertiären Hydroxylgruppen im Polyol bedeutet und im Bereich von 0 bis 7 liegt, wobei die Gesamtzahl von a + c im Bereich von 3 bis 8 liegt, n gleich oder größer a ist, und wobei mehr als 95 % der primären Hydroxylgruppen im Polyol im Produkt durch sekundäre oder tertiäre Hydroxylgruppen ersetzt werden, mit (B) b Mol, pro Mol des Produktes, einer Fettsäure der Formel RCOOH, worin R 7 bis 23 Kohlenstoffatome aufweist und b größer als 2 aber nicht größer als a + c ist.

2. Verwendung nach Anspruch 1, worin n ausreichend ist, um eine Lipasehydrolysegeschwindigkeit von weniger als etwa 10 % im Vergleich zu Olivenöl auszuüben.

3. Verwendung nach Anspruch 1 oder 2, worin n einen durchschnittlichen Wert im Bereich von 2 bis 8 aufweist.

4. Verwendung nach einem der Ansprüche 1 bis 3, bei der R von ausreichender Länge ist, daß die Mischung von epoxidverlängerten Polyolester im wesentlichen widerstandsfähig gegen die Absorption im Verdauungstrakt ist.

5. Verwendung nach Anspruch 4, worin R aus C_{13-17} Ketten und Mischungen davon ausgewählt ist.

6. Verwendung nach einem der Ansprüche 1 bis 5, worin das Epoxid aus Propylenoxid, Pentenoxid, 1,2-Epoxybutan, 2,3-Epoxybutan, 1,2-Epoxi-2-methylpropan, 1,2-Epoxi-cyclohexan und Mischungen davon ausgewählt ist.

7. Verwendung nach einem der Ansprüche 1 bis 6, worin das Polyol aus Zucker, Glycerin, Sacchariden und Mischungen davon ausgewählt ist.

8. Verwendung nach Anspruch 7, worin der Zucker aus Glukose, Mannose, Galactose, Arabinose, Xylose, Sorbitose, Amylose und Mischungen davon ausgewählt ist.

9. Verwendung nach einem der Ansprüche 1 bis 8, worin $P(OH)_{a+c}$ Glycerin ist, a 2 ist, c 1 ist, das Epoxid aus Propylenoxid, Butylenoxid und Isobutylenoxid ausgewählt ist, n einen durchschnittlichen Wert von 2 bis 8 aufweist und b einen durchschnittlichen Wert aufweist, der größer als 2 aber nicht größer als 3 ist.

10. Verwendung nach Anspruch 9, worin n im Bereich von 2 bis 5, vorzugsweise 3 bis 5 liegt und b 3 ist.

11. Verwendung nach einem der Ansprüche 1 bis 10, worin die Mischung durch ein Verfahren hergestellt wurde, bei dem man:

a) das Polyol der Formel $P(OH)_{a+c}$ in Gegenwart eines Basenkatalysators mit dem C_{3-6}-Epoxid für einen Zeitraum der ausreicht, um eine Mischung von polyepoxidverlängerten Polyolen mit einer Minimum-Epoxilierung-Index-Durchschnittszahl n, die nicht kleiner als a ist und worin mehr als 95 % der primären Hydroxylgruppen der Polyole in sekundäre oder tertiäre Hydroxylgruppen überführt wurden, umsetzt,

b) die Mischung aus epoxidverlängerten Polyolen mit mindestens einer Fettsäure (RCOOH) zur Herstellung der Mischung von epoxidverlängerten Polyolester umsetzt.

12. Verwendung nach Anspruch 11, worin das Verfahren die folgenden Schritte enthält:

a) Spaltung eines natürlichen Fettes oder Öles ausgewählt aus Sojabohnenöl, Rapsöl, Talg, Leinsamenöl, Kokosnußöl, Palmöl, Babassuöl, Maisöl, Fettöl, Fischöl, Olivenöl, Erdnußöl, Saflorsamenöl, Sesamsamenöl, Jojobaöl und Sonnenblumensamenöl und Mischungen davon zur Bildung von Glycerin und einer oder mehrerer Fettsäuren RCOOH, worin R eine C_{7-23} Gruppe ist;

b) Abtrennen des Glycerins von der Fettsäure und

c) Verwendung des Glycerins in der basenkatalysierten Additionsreaktion von Anspruch 11.

13. Verwendung nach Anspruch 12, worin $P(OH)_{a+c}$ Glycerin ist, a 2 ist, c 1 ist, das Epoxid Propylenoxid ist, n einen durchschnittlichen Wert über 2,2 aufweist und b einen durchschnittlichen Wert über 2 jedoch nicht mehr als 3 besitzt.

14. Verwendung nach Anspruch 12, worin $P(OH)_{a+c}$ Glycerin ist, a 2 ist, c 1 ist, das Epoxid aus Butylenoxid und Isobutylenoxid ausgewählt ist, n einen durchschnittlichen Wert von 2 bis 8 aufweist und b einen durchschnittlichen Wert aufweist der über 2 jedoch nicht über 3 beträgt.

15. Eßbare Zusammensetzung enthaltend Bestandteile vom Fett- und Nicht-Fett-Typ und worin mindestens ein Teil des Fett-Typ-Materials der Zusammensetzung eine Mischung von epoxidverlängerten Polyolester enthält, erhältlich durch Reaktion von (A) dem Produkt aus der Reaktion von n Mol eines C_{3-6}-Epoxids pro Mol eines Polyols mit der Formel $P(OH)_{a+c}$, worin a die Zahl der primären Hydroxylgruppen im Polyol ist und im Bereich von 1 bis 8 liegt, c die Gesamtzahl der sekundären und tertiären Hydroxylgruppen im Polyol bedeutet und im Bereich von 0 bis 7 liegt, wobei die Gesamtzahl von a + c im Bereich von 3 bis 8 liegt, n gleich oder größer als a ist, und mehr als 95 % der Hydroxylgruppen im Polyol im Produkt durch sekundäre oder tertiäre Hydroxylgruppen ersetzt sind, mit (B) b Mol, pro Mol des Produktes, einer Fettsäure mit der Formel RCOOH, worin R 7 bis 23 Kohlenstoffatome aufweist und b größer als 2 aber nicht größer als a + c ist.

16. Eßbare Zusammensetzung nach Anspruch 15, in Form eines Salatdressings, Margarine, Buttermischung, Mayonnaise oder Backfett.

17. Zusammensetzung enthaltend eine Mischung aus Fett-Typ-Bestandteilen geeignet zur Verwendung als Kochöl oder Fett oder zur Herstellung von Nahrungsmittelzusammensetzungen mit niedrigem Kaloriengehalt, wobei die Mischung ein eßbares Öl oder Fett und mindestens 10 Gew.%, bezogen auf das Gesamtgewicht der Mischung, einer Mischung aus epoxidverlängerten Polyolester erhältlich durch die Reaktion von (A) dem Produkt aus der Reaktion von n Mol eines C_{3-6} Epoxids pro Mol eines Polyols mit der Formel $P(OH)_{a+c}$, worin a die Zahl der primären Hydroxylgruppen im Polyol ist und im Bereich von 1 bis 8 liegt, c die Gesamtzahl der sekundären und tertiären Hydroxylgruppen im Polyol ist und im Bereich von 0 bis 7 liegt, wobei die Gesamtzahl von a + c im Bereich von 3 bis 8 liegt, n gleich oder größer als a ist, und mehr als 95 % der primären Hydroxylgruppen im Polyol im Produkt durch sekundäre oder tertiäre Hydroxylgruppen ersetzt sind, mit (B) b Mol, pro Mol des Produktes, einer Fettsäure mit der Formel RCOOH, worin R 7 bis 23 Kohlenstoffatome aufweist und b größer als 2 aber nicht größer als a + c ist.

18. Zusammensetzung nach einem der Ansprüche 15 bis 17, worin n ausreicht, eine Lipasehydrolysegeschwindigkeit von weniger als etwa 10 % im Vergleich zu Olivenöl auszuüben.

19. Zusammensetzung nach einem der Ansprüche von 15 bis 18, worin n eine durchschnittliche Zahl im Bereich von 2 bis 8 ist.

20. Zusammensetzung nach einem der Ansprüche 15 bis 19, worin R von ausreichender Länge ist, daß die Mischung von epoxidverlängerten Polyolester im wesentlichen einer Absorption im Verdauungstrakt widersteht.

21. Zusammensetzung nach Anspruch 20, worin R aus C_{3-17} Ketten und Mischungen davon ausgewählt ist.

22. Zusammensetzung nach einem der Ansprüche 15 bis 21, worin das Epoxid aus Propylenoxid, Pentenoxid, 1,2-Epoxybutan, 2,3-Epoxybutan, 1,2-Epoxy-2-ethylpropan, 1,2-Epoxy-cyclohexan und Mischungen davon ausgewählt ist.

23. Verwendung nach einem der Ansprüche 1 bis 6, worin das Polyol aus Zucker, Glycerin, Sacchariden und Mischungen davon ausgewählt ist.

24. Zusammensetzung nach Anspruch 23, worin der Zucker aus Glukose, Mannose, Galactose, Arabinose, Xylose, Sorbitose, Amylose und Mischungen davon ausgewählt ist.

25. Zusammensetzung nach einem der Ansprüche 15 bis 24, worin $P(OH)_{a+c}$ Glycerin ist, a 2 ist, c 1 ist, das Epoxid aus Propylenoxid, Butylenoxid und Isobutylenoxid ausgewählt ist, n einen durchschnittlichen Wert von 2 bis 8 aufweist und b einen durchschnittlichen Wert aufweist, der größer als 2 aber nicht größer als 3 ist.

26. Zusammensetzung nach Anspruch 15, worin n im Bereich von 2 bis 5, vorzugsweise 3 bis 5 liegt und b 3 ist.

27. Zusammensetzung nach einem der Ansprüche 15 bis 26 worin die Mischung durch ein Verfahren hergestellt wurde, bei dem man:
   a) das Polyol der Formel $P(OH)_{a+c}$ in Gegenwart eines Basenkatalysators mit dem C_{3-6} Epoxid für einen Zeitraum umsetzt, der ausreicht, um eine Mischung aus polyepoxidverlängerten Polyolen mit einer minimalen Epoxilierungs-Index-Durchschnittszahl n zu ergeben, die nicht kleiner als a ist, und worin mehr als 95 % der primären Hydroxylgruppen der Polyole in sekundäre oder tertiäre Hydroxylgruppen umgewandelt sind, und
   b) die Mischung aus epoxidverlängerten Polyolen mit mindestens einer Fettsäure RCOOH, umsetzt, um die Mischung aus epoxidverlängerten Polyolester herzustellen.

28. Zusammensetzung nach Anspruch 27, worin das Verfahren die folgenden Schritte enthält:
   a) Spaltung eines natürlichen Fettes oder Öles ausgewählt aus Sojabohnenöl, Rapsöl, Talg, Leinsamenöl, Kokosnußöl, Palmöl, Babassuöl, Maisöl, Fettöl, Fischöl, Olivenöl, Erdnußöl, Saflorsamenöl, Sesamsamenöl, Jojobaöl und Sonnenblumensamenöl und Mischungen davon zur Bildung von Glycerin und einer oder mehrerer Fettsäuren RCOOH, worin R eine C_{7-23} Gruppe ist;
   b) Abtrennen des Glycerins von der Fettsäure und
   c) Verwendung des Glycerins in der basenkatalysierten Additionsreaktion von Anspruch 11.

29. Zusammensetzung nach Anspruch 28, worin $P(OH)_{a+c}$ Glycerin ist, a 2 ist, c 1 ist, das Epoxid Propylenoxid ist, n einen durchschnittlichen Wert von mehr als 2,2 aufweist und b einen durchschnittlichen Wert von mehr als 2, jedoch nicht mehr als 3 aufweist.

30. Zusammensetzung nach Anspruch 12, worin $P(OH)_{a+c}$ Glycerin ist, a 2 ist, c 1 ist, das Epoxid aus Butylenoxid und Isobutylenoxid ausgewählt ist, n einen Durchschnittswert von 2 bis 8 aufweist und b einen Durchschnittswert aufweist, der größer 2 jedoch nicht größer 3 ist.

Revendications

1. Utilisation, en tant que succédané de valeur nutritive réduite de graisse ou d'huile comestible, d'un mélange d'esters de polyols à prolongements époxyde pouvant être obtenu par la réaction de : (A) le produit de réaction de $\underline{n}$ moles d'un époxyde en C_{3-6} par mole d'un polyol ayant la formule $P(OH)_{a+c}$ dans laquelle $\underline{a}$ est le nombre de groupes hydroxy primaires dans le polyol et est dans la gamme de 1 à 8, $\underline{c}$ est le nombre total de groupes hydroxy secondaires et tertiaires dans le polyol et est dans la

gamme de 0 à 7, le total de a + c étant dans la gamme de 3 à 8, n est égal ou supérieur à a, et plus de 95% des groupes hydroxy primaires dans le polyol sont remplacés dans ce produit par des groupes hydroxy secondaires ou tertiaires, avec (B) b moles par mole de ce produit, d'un acide gras ayant la formule RCOOH dans laquelle R contient 7 à 23 atomes de carbone et b est supérieur à 2 mais ne dépasse pas a + c.

2. Utilisation suivant la revendication 1 dans laquelle n est suffisant pour conférer une vitesse d'hydrolyse de lipase de moins d'environ 10% par rapport à l'huile d'olive.

3. Utilisation suivant les revendications 1 ou 2, dans laquelle n a une valeur moyenne dans la gamme de 2 à 8.

4. Utilisation suivant l'une quelconque des revendications 1 à 3, dans laquelle R est d'une longueur suffisante pour que le mélange d'esters de polyols à prolongements époxyde soit notablement résistant à l'absorption par les voies digestives.

5. Utilisation suivant la revendication 4, dans laquelle R est choisi parmi les chaînes en C_{13-17} et leurs mélanges.

6. Utilisation suivant l'une quelconque des revendications 1 à 5, dans laquelle l'époxyde est choisi parmi l'oxyde de propylène, l'oxyde de pentylène, le 1,2-époxybutane, le 2,3-époxybutane, le 1,2-époxy-2-méthylpropane, le 1,2-époxy-cyclohexane et leurs mélanges.

7. Utilisation suivant l'une quelconque des revendications 1 à 6, dans laquelle le polyol est choisi parmi les sucres, le glycérol, les saccharides et leurs mélanges.

8. Utilisation suivant la revendication 7, dans laquelle le sucre est choisi parmi le glucose, le mannose, le galactose, l'arabinose, le xylose, le sorbitose, l'amylose et leurs mélanges.

9. Utilisation suivant l'une quelconque des revendications 1 à 8, dans laquelle $P(OH)_{a+c}$ est le glycérol, a est 2, c est 1, l'époxyde est choisi parmi l'oxyde de propylène, l'oxyde de butylène et l'oxyde d'isobutylène, n a une valeur moyenne de 2 à 8, et b a une valeur moyenne qui est supérieure à 2 mais ne dépasse pas 3.

10. Utilisation suivant la revendication 9, dans laquelle n est dans la gamme de 2 à 5, de préférence de 3 à 5, et b est 3.

11. Utilisation suivant l'une quelconque des revendications 1 à 10, dans laquelle ce mélange a été préparé par un procédé comprenant les étapes de :
    a) réaction de ce polyol de formule $P(OH)_{a+c}$ en présence d'une base comme catalyseur, avec cet époxyde en C_{3-6}, pendant une période de temps suffisante pour fournir un mélange de polyols à prolongements polyépoxyde ayant un nombre moyen d'indice d'époxylation minimum n qui n'est pas inférieur à a et dans lequel plus de 95% des groupes hydroxy primaires de ces polyols sont convertis en groupes hydroxy secondaires ou tertiaires; et
    b) réaction de ce mélange de polyols à prolongements époxyde avec au moins un tel acide gras RCOOH, pour produire ce mélange d'esters de polyols à prolongements époxyde.

12. Utilisation suivant la revendication 11, dans laquelle ce procédé comprend les étapes de :
    a) coupure d'une graisse ou d'une huile naturelle choisie parmi une huile de soja, une huile de colza, une huile de coton, du suif, une huile de coco, une huile de palme, une huile de babassu, une huile de maïs, du lard, une huile de poisson, une huile d'arachide, une huile de carthame, une huile de sésame, une huile de jojoba et une huile de tournesol et leurs mélanges, pour former du glycérol et un ou plusieurs acides gras RCOOH dans lesquels R est un groupe en C_{7-23};
    b) séparation du glycérol de cet acide gras; et
    c) utilisation de ce glycérol dans la réaction d'addition catalysée par une base de la revendication 11.

13. Utilisation suivant la revendication 12, dans laquelle $P(OH)_{a+c}$ est le glycérol, a est 2, c est 1, l'époxyde est l'oxyde de propylène, n a une valeur moyenne supérieure à 2,2, et b a une valeur moyenne supérieure à 2 mais qui ne dépasse pas 3.

14. Utilisation suivant la revendication 12, dans laquelle $P(OH)_{a+c}$ est le glycérol, a est 2, c est 1, l'époxyde est choisi parmi l'oxyde de butylène et l'oxyde d'isobutylène, n a une valeur moyenne de 2 à 8, et b a une valeur moyenne qui est supérieure à 3 mais ne dépasse pas 3.

15. Composition comestible contenant des composants de type gras et de type non gras, et dans laquelle une partie au moins de la matière de type non gras de la composition comprend un mélange d'esters de polyols à prolongements époxyde pouvant être obtenu par la réaction de : (A) le produit de réaction de n moles d'un époxyde en C_{3-6} par mole d'un polyol ayant la formule $P(OH)_{a+c}$ dans laquelle a est le nombre de groupes hydroxy primaires dans le polyol et est dans la gamme de 1 à 8, c est le nombre total de groupes hydroxy secondaires et tertiaires dans le polyol et est dans la gamme de 0 à 7, le total de a+c étant dans la gamme de 3 à 8, n est égal ou supérieur à a, et plus de 95% des groupes hydroxy primaires dans le polyol sont remplacés dans ce produit par des groupes hydroxy secondaires ou tertiaires, avec (B) b moles par mole de ce produit, d'un acide gras ayant la formule RCOOH dans laquelle R contient 7 à 23 atomes de carbone et b est supérieur à 2 mais ne dépasse pas a+c.

16. Composition comestible suivant la revendication 15, qui est un assaisonnement pour salades, une margarine, un mélange de beurre, une mayonnaise ou une matière grasse.

17. Composition comprenant un mélange de composants de type gras utilisable comme huile ou graisse de cuisine ou dans la préparation de compositions alimentaires de faible valeur nutritive, ce mélange comprenant une huile ou une graisse comestible et au moins 10% en poids, par rapport au poids total du mélange, d'un mélange d'esters de polyols à prolongements époxyde pouvant être obtenu par la réaction de : (A) le produit de réaction de n moles d'un époxyde en C_{3-6} par mole d'un polyol ayant la formule $P(OH)_{a+c}$ dans laquelle a est le nombre de groupes hydroxy primaires dans le polyol et est dans la gamme de 1 à 8, c est le nombre total de groupes hydroxy secondaires et tertiaires dans le polyol et est dans la gamme de 0 à 7, le total de a+c étant dans la gamme de 3 à 8, n est égal ou supérieur à a, et plus de 95% des groupes hydroxy primaires dans le polyol sont remplacés dans ce produit par des groupes hydroxy secondaires ou tertiaires, avec (B) b moles par mole de ce produit, d'un acide gras ayant la formule RCOOH dans laquelle R contient 7 à 23 atomes de carbone et b est supérieur à 2 mais ne dépasse pas a+c.

18. Composition suivant l'une quelconque des revendications 15 à 17, dans laquelle n est suffisant pour conférer une vitesse hydrolyse de lipase de moins d'environ 10% par rapport à l'huile d'olive.

19. Composition suivant l'une quelconque des revendications 15 à 18, dans laquelle n a une valeur moyenne dans la gamme de 2 à 8.

20. Composition suivant l'une quelconque des revendications 15 à 19, dans laquelle R est d'une longueur suffisante pour que le mélange d'esters de polyols à prolongements époxyde soit notablement résistant à l'absorption par les voies digestives.

21. Composition suivant la revendication 20, dans laquelle R est choisi parmi les chaînes en C_{13-17} et leurs mélanges.

22. Composition suivant l'une quelconque des revendications 15 à 21, dans laquelle l'époxyde est choisi parmi l'oxyde de propylène, l'oxyde de pentylène, le 1,2-époxybutane, le 2,3-époxybutane, le 1,2-époxy-2-méthylpropane, le 1,2-époxy-cyclohexane et leurs mélanges.

23. Composition suivant l'une quelconque des revendications 15 à 22, dans laquelle le polyol est choisi parmi les sucres, le glycérol, les saccharides et leurs mélanges.

24. Composition suivant la revendication 23, dans laquelle le sucre est choisi parmi le glucose, le mannose, le galactose, l'arabinose, le xylose, le sorbitose, l'amylose et leurs mélanges.

25. Composition suivant l'une quelconque des revendications 15 à 24, dans laquelle $P(OH)_{a+c}$ est le glycérol, a est 2, c est 1, l'époxyde est choisi parmi l'oxyde de propylène, l'oxyde de butylène et l'oxyde d'isobutylène, n a une valeur moyenne de 2 à 8, et b a une valeur moyenne qui est supérieure à 2 mais ne dépasse pas 3.

26. Composition suivant la revendication 25, dans laquelle n est dans la gamme de 2 à 5, de préférence de 3 à 5, et b est 3.

27. Composition suivant l'une quelconque des revendications 15 à 26, dans laquelle ce mélange a été préparé par un procédé comprenant les étapes de :

a) réaction de ce polyol de formule $P(OH)_{a+c}$ en présence d'une base comme catalyseur, avec cet époxyde en C_{3-6}, pendant une période de temps suffisante pour fournir un mélange de polyols à prolongements polyépoxyde ayant un nombre moyen d'indice d'époxylation minimum n qui n'est pas inférieur à a et dans lequel plus de 95% des groupes hydroxy primaires de ces polyols sont convertis en groupes hydroxy secondaires ou tertiaires; et

b) réaction de ce mélange de polyols à prolongements époxyde avec au moins un tel acide gras RCOOH, pour produire ce mélange d'esters de polyols à prolongements époxyde.

28. Composition suivant la revendication 27, dans laquelle ce procédé comprend les étapes de :

a) coupure d'une graisse ou d'une huile naturelle choisie parmi une huile de soja, une huile de colza, une huile de coton, du suif, une huile de coco, une huile de palme, une huile de babassu, une huile de maïs, du lard, une huile de poisson, une huile d'arachide, une huile de carthame, une huile de sésame, une huile de jojoba et une huile de tournesol et leurs mélanges, pour former du glycérol et un ou plusieurs acides gras RCOOH dans lesquels R est un groupe en C_{7-23};

b) séparation du glycérol de cet acide gras; et

c) utilisation de ce glycérol dans la réaction d'addition catalysée par une base de la revendication 11.

29. Composition suivant la revendication 28, dans laquelle $P(OH)_{a+c}$ est le glycérol, a est 2, c est 1, l'époxyde est l'oxyde de propylène, n a une valeur moyenne supérieure à 2,2 et b a une valeur moyenne supérieure a 2 mais qui ne dépasse pas 3.

30. Composition suivant la revendication 28, dans laquelle $P[OH]_{a+c}$ est le glycérol, a est 2, c est 1, l'époxyde est choisi parmi l'oxyde de butylène et l'oxyde d'isobutylène, n a une valeur moyenne de 2 à 8, et b a une valeur moyenne qui est supérieure à 3 mais ne dépasse pas 3.